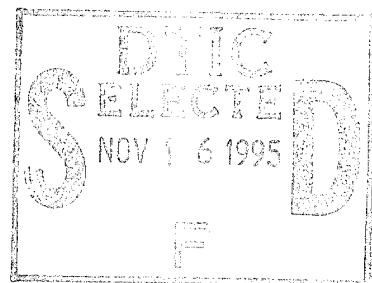




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Sacramento CA 95813-6000

19 October 1995
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Office of Naval Research
Code 251 JWK
Ballston Tower One
800 North Quincy Street
Arlington, VA 22217-5660

Attention: Ms. Joyce Keller

Subject: Contract N00014-93-C-0068, Final Report

Dear Ms. Keller:

Enclosed is the Final Report for Contract N00014-93-C-0068, Processable Fluorine-Containing Poly (Ether-Urethane) Elastomers for Fouling Release Coatings.

If you have any questions regarding this report, please contact either Mr. Jim Klier at (916) 355-5809 or the undersigned at (916) 355-2840.

Best regards,

Carolyne S. Montgomery
Carolyne S. Montgomery
Contract Manager
Specialty Chemicals and Materials

CSM:lmw

Enclosure

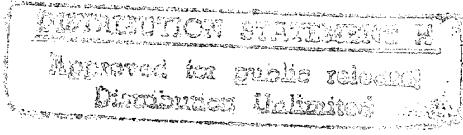
cc: Dr. Kenneth J. Wynne (1 copy)
Director, Naval Research Laboratory (1 copy)
Defense Technical Information Center (2 copies)
DCMO Sacramento (1 Copy)

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REPORT DOCUMENTATION PAGE

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6. AUTHOR(S) Aslam Malik, Roland P. Carlson					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Aerojet Chemicals and Materials Division P. O. Box 13222 Sacramento, CA 95813-6000			8. PERFORMING ORGANIZATION REPORT NUMBER		
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13. ABSTRACT (Maximum 200 words) A new family of fluorinated polyether urethanes, based on a novel polyether polyol with fluorinated side chains, was prepared and characterized by surface, mechanical and thermal property measurements. These new materials are elastomers and are characterized by low surface energy, high hydrophobicity, low glass transition temperature, and excellent bonding properties. In addition to high abrasion resistance and low coefficient of friction, coatings prepared from these materials exhibit fouling release characteristics.					
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CONTRACT: N00014-93-C-0068

R&T Code: 4132087

ONR Program Manager: Dr. Kenneth J. Wynne

FINAL REPORT

**PROCESSABLE FLUORINE-CONTAINING POLY(ETHER-URETHANE)
ELASTOMERS FOR FOULING RELEASE COATINGS**

by

Aslam A. Malik and Roland P. Carlson

Aerojet
Chemical and Materials Division
P.O. Box 13222
Sacramento, CA 95813-6000

October 4, 1995

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Objective

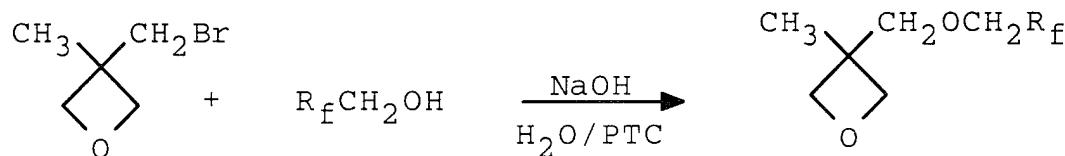
Our primary objective is to develop a novel fluoropolymer system that will enable us to study the effect of basic polymer properties on adhesion of marine organism to polymeric surfaces. Our ultimate goal is to use these properties to design a coating material that is intrinsically fouling resistant and will inhibit settlement or facilitate removal of fouling organism by simple cleaning methods.

Approach

We will develop a new series of fluorinated polyurethane elastomers that are characterized by low glass transition temperature and by their ability to form coatings with low surface energy. We will prepare and polymerize oxetane monomers substituted at the 3-position with fluoroalkyl groups to give hydroxy-terminated prepolymers with flexible polyether backbone and fluorinated side chains. The primary hydroxy groups will then be reacted with polyisocyanates to give polyether-urethane elastomers. In the proposed system, the flexible polyether backbone will dictate the glass transition temperature and the pendant fluorinated side chains will control the surface properties of the polymer. We will study the fundamental properties of the polymer and determine how these properties affect fouling. We will study the variation in the surface properties as a function of structure and length of the fluorinated side chain, and study the effect of physical changes such as modulus, elongation, and flexibility of the polymer backbone on fouling.

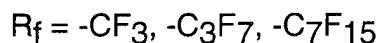
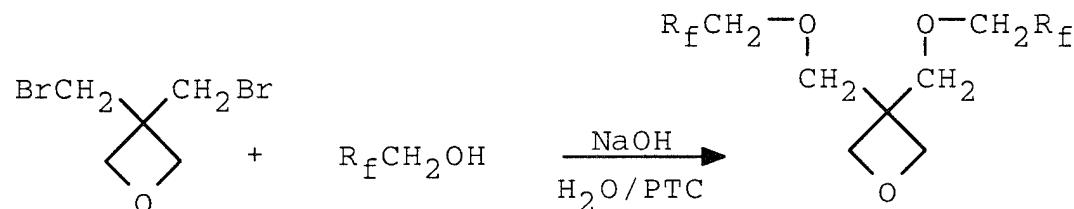
Results

Oxetanes substituted at the 3-position with fluoroalkoxy side chain of the general structure-- $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{OCH}_2-$ where $n = 0, 1, 2,$ and 6 --were prepared in 85-90% yields by reacting 3-bromomethyl-3-methyloxetane with 1H,1H-perfluoroalkanols in aqueous sodium hydroxide under phase transfer catalysis. *In this process no organic solvent is used.*

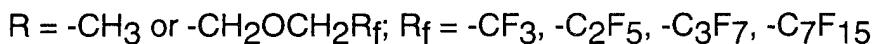
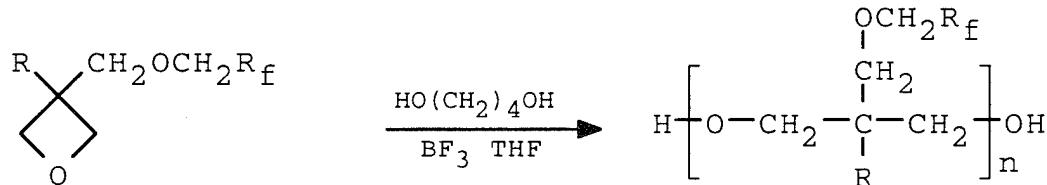


$$R_f = -\text{CF}_3, -\text{C}_2\text{F}_5, -\text{C}_3\text{F}_7, -\text{C}_7\text{F}_{15}$$

Oxetane monomers with two fluorinated side chains were similarly prepared by reacting 3,3-bis(bromomethyl)oxetane with 1H,1H-perfluoroalkanols. The oxetane monomers were purified by distillation and only monomers that were >99% pure by glc were used in the subsequent polymerization.



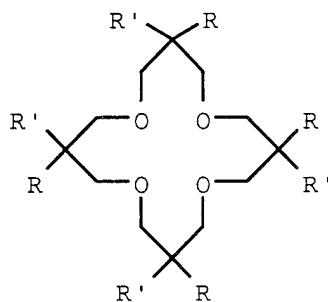
The fluorinated oxetane (Fox) monomers were then polymerized in methylene chloride or a mixture of methylene chloride and Freon 113, in the presence of a Lewis acid catalyst and an alcohol initiator to give the corresponding hydroxy-terminated prepolymers (Poly Fox polyol) in 90-95% yield .



The preferred initiator and Lewis acid catalysts are 1,4-butanediol and boron trifluoride tetrahydrofuranate (BF_3 THF), respectively. The prepolymers were characterized by NMR ($^1\text{H}, ^{13}\text{C}, ^{19}\text{F}$), GPC, and equivalent weight determinations. Traditional catalysts such as, boron trifluoride etherate (BF_3 etherate), promote $-\text{CH}_2\text{F}$ and $-\text{CH}_2\text{CH}_3$ termination, and in some cases, reduce the functionality of the prepolymer by as much as 32%. A new process, employing BF_3 THF as a catalyst, eliminates the formation of mono-functional materials and gives prepolymers with an average functionality of 1.94.

The molecular weight of the prepolymer is dependent on factors such as, monomer: initiator ratio, temperature, reactivity of the monomer, rate of addition, and concentration. By carefully controlling these parameters it is possible to prepare prepolymers with molecular weights ranging from 2,000 daltons to about 30,000 daltons. GPC analysis of the prepolymers reveal a unimodal molecular weight distribution with

Polydispersities ranging between 1.32 and 1.65. Prepolymers, as isolated, are contaminated with 3% to 5% of a cyclic tetramer. The amount of cyclic tetramer, however, is reduced to below 0.5% by precipitating the prepolymer from methanol. The cyclic tetramer is a fluorinated crown ether, and has been isolated and characterized by NMR, mass spectra, and combustion analysis.



R = CH₃ or R' = -C₃F₇

Equivalent weight of the prepolymers was determined by ¹H NMR end group analysis, p-toluenesulfonyl isocyanate/dibutylamine titration, and by isocyanate cure. The preferred method is end group analysis by ¹H NMR, since it is simple, fast, reliable, and only requires a small amount of sample for analysis. Moreover, the correlation between the equivalent weight determined by ¹H NMR and the equivalent weight determined by the isocyanate cure is excellent. A variety of end capping agents were screened for end group analysis by ¹H NMR: trifluoroacetic anhydride (TFAA), trimethylacetyl chloride, trichloroacetyl isocyanate, p-toluenesulfonyl isocyanate, and p-nitrophenyl isocyanate. TFAA is the end capping agent of choice since it is cheap, is simple to handle, and does not exhibit any signals in ¹H NMR.

The prepolymers derived from oxetane monomers with one fluorinated side chain are amorphous oils. The glass transition temperatures of these prepolymers, as determined by DSC, are in the neighborhood of -40 to -49°C. Only a minor dependence of glass transition temperature on the length of the side chain is observed (Table 1). The prepolymers derived from oxetane monomers with two symmetrical fluorinated side chains are crystalline and exhibit a sharp endothermic transition in DSC (melting point) at ca. 80°C. Thermal stability of these prepolymers in air, as determined by TGA, is in the neighborhood of 220-230°C.

Table 1. Glass Transition Temperature of FOX Prepolymers

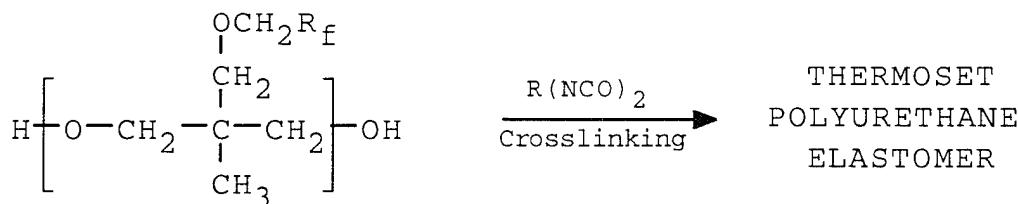
Prepolymer	T _g (°C)
Poly 3-Fox	-41
Poly 3/7-Fox (25:75)	-42
Poly 7-Fox	-45
Poly 3/15-Fox (25:75)	-48
Poly 15-Fox	-49

¹ Glass transition temperatures were measured by DSC at 10°C/min under nitrogen

The solubility of Poly Fox polyols in organic solvents is dependent on the length of the fluorinated side chain and on the molecular weight of the polyol. High molecular weight prepolymers with long fluorinated side chains are soluble only in select organic solvents, whereas low molecular weight prepolymers with short fluorinated side chains are soluble in most organic solvents.

A variety of co-prepolymers were also prepared by co-polymerizing Fox monomers with both fluorinated and non-fluorinated oxetane monomers. For example, 3-(heptafluoro-butoxymethyl)-3-methyloxetane (7-Fox) copolymerizes readily with tetrahydrofuran to give a polyol that is an amorphous oil. Copolymerization is conducted in THF and in contrast to the process used in synthesis of homo-prepolymers, *no fluorinated or chlorinated solvents are used in the synthesis of Fox/THF co-prepolymers*. We have prepared a series of Fox/THF co-prepolymers with THF content varying between 5% to 70 mole% THF. ¹³C NMR analysis reveal that Fox/THF co-prepolymers are random copolymers with no apparent block structure. Also, Poly 7-Fox/THF co-prepolymers are more soluble and relatively more compatible with non-fluorinated materials than the corresponding homo-prepolymers.

Thermoset fluorinated polyether-urethane elastomers are prepared by reacting the amorphous fluorinated polyether diols with diisocyanate such as, hexamethylene diisocyanate, isophorone diisocyanate, MDI, and hydrogenated MDI, in the presence of a low molecular weight crosslinking agent such as, trimethylolpropane, Isonol 93, or Jeffamine. The preferred catalysts are DABCO (LV-33) and dibutyltin dilaurate.



$\text{R}_f = -\text{CF}_3, -\text{C}_2\text{F}_5, -\text{C}_3\text{F}_7, -\text{C}_7\text{F}_{15}$

These cross linked materials are tack free, relatively soft, elastomers with low tensile modulus and high elongation. If desired, the modulus and hardness can be increased by increasing the cross link density and by increasing the amount of hard segment. These polyurethane elastomers exhibit good resistance towards common organic solvents, but are not stable towards strong acids, and exhibit swelling in THF and Freon 113. The glass transition temperatures of the polyurethane elastomers, as measured with DSC and by dynamic mechanical analysis, are in the neighborhood of -45°C . These values are almost identical to those observed for the fluorinated polyol soft segment, thus indicating a good phase separation between the fluorinated and the non-fluorinated segments.

The contact angle of Poly Fox urethane elastomer with distilled water was determined by both static and dynamic contact angle analysis. The results of this study are summarized in Table 2. The static contact angle is dependent on the length of the fluorinated side chain and varies between 110° and 137° . A large hysteresis is observed between advancing and receding contact angles in dynamic contact angle analysis. For example, the advancing contact angle of water with Poly 7-Fox/IPDI/Isonol-93 urethane is 114° , whereas the receding contact angle is only 64° .

Table 2. Contact Angle Analysis

Polyurethane	Static	Dynamic	
		Advancing	Receding
Poly 3-Fox Urethane	108°	108°	59°
Poly 3/7-Fox (50:50) Urethane	109°	-	-
Poly 7-Fox Urethane	116°	114°	64°
Poly 3/15 Fox (25:75) Urethane	128°	-	-
Poly 15-Fox Urethane	135°	-	-

Surface energy of select fluorinated polyurethane elastomers was measured by the method of Wu et al. The surface energy of Poly 7-Fox/IPDI/Isonol-93 urethane was 13.5 ergs/cm², whereas that of Poly 7-Fox/THF (67:33)/IPDI/Isonol-93 was 15.0 ergs/cm². For comparison, the surface energy of Teflon is 18.5 ergs/cm². The extremely low surface energy of Poly 7-Fox urethanes, as compared to Teflon, suggests that these materials should exhibit good release characteristics. Poly 7-Fox urethane was also characterized by AT-IR and by ESCA analysis. The analyses reveal that the polymer surface is enriched with fluorine as compared to the bulk and functional groups, such as urethane, are not present at the polymer/air interface. The amount of fluorine at the surface, however, is lower than the amount calculated for a polymer surface saturated with perfluoroalkyl groups.

Even though Poly Fox-urethanes exhibit extremely low surface energies, they bond extremely well to substrates such as aluminum, steel, and graphite. The bonding of Poly 7-Fox urethane to steel is so strong that cohesive failure in the coating is observed in most cases. Results from peel strength analysis reveal that Poly 7-Fox urethane exhibit bonding characteristics of conventional polyurethanes. Fluorinated polyether-urethanes can be processed as thin coatings or as bulk articles by employing traditional polyurethane processing techniques. Coatings prepared from these fluorinated materials exhibit high abrasion resistance and relatively low coefficient of friction as compared to non-fluorinated polyurethanes.

Three stainless steel panels, coated with experimental polyurethane formulation prepared from Poly 3/7-Fox and Poly 7-Fox diols were submitted to Dr. Jim Griffith at NRL for preliminary evaluation as fouling release coatings. The test panels were submerged in Chesapeake bay for about 6 months and on removal were tested for release of barnacles and soft foulers. The soft foulers were released readily whereas barnacles were removed with increasing finger pressure. The barnacles were released whole with basal plates intact. Also, the fluorinated polyurethanes did not undergo any degradation and behaved as tough elastomers after 6 month immersion in Chesapeake Bay water.

Conclusions

A new family of fluorinated polyether-urethane (Poly Fox) elastomers has been prepared by a simple, environmentally friendly, three step process from relatively inexpensive raw materials.

The hydroxy-terminated fluorinated prepolymer is a colorless, amorphous oil with a highly flexible polyether backbone and is ideally suited as a soft block for segmented polyurethane elastomers.

The molecular weight of the prepolymer is dependent on factors such as monomer: initiator ratio, temperature, reactivity of the monomer, etc., and can be varied between 2000 and 30,000 daltons.

Poly Fox urethanes exhibit extremely low surface energy, good mechanical properties, low glass transition temperature, high hydrophobicity, and outstanding adhesion to substrates.

Poly Fox urethanes can be processed into thin coatings or bulk articles. The coating prepared from these materials exhibit high abrasion resistance and low coefficient of friction.

The mechanical properties of Poly Fox urethanes can be varied by changing the molecular weight and functionality of the fluorinated prepolymer, cross link density, and the type of curing/crosslinking agent.

In Poly Fox urethane, fluorine is present in the side-chain. This facilitates the orientation of the fluorinated side chains towards the polymer/air interface and thus provides a surface that is enriched in fluorine, as compared to the bulk.

The surface properties of Poly Fox urethanes is highly dependent on the length of the fluorinated side chain. Fluorinated side chains longer than $-C_3F_7$ are needed to provide optimum enrichment of the polymer surface with fluorine.

Preliminary test results indicate that Poly Fox urethanes exhibit fouling release characteristics. These materials are tough elastomers and do not degrade after 6 month immersion in Chesapeake bay water.

Low surface energy is not the only important criteria in the development of fouling release coatings. Other factors such as, low glass transition temperature, mobility of the polymer chains, low modulus, and stability of the coating in water (low contact angle hysteresis) are equally important.

Part B

- a. List of all Undergraduates, Graduate, and Post-doctoral associates: None
- b. List of all publications, patents, and reports:

Publications

T. Ho, A. A. Malik, K.J. Wynne, T. J. McCarthy, K. H.-Z. Zhuang, K. Baum, and R. V. Honeychuck " Polyurethanes Based on Fluorinated Diols", Chapter in *Advances in Step growth Polymerization*, Am. Chem. Soc. Symposium Series, J. Hedrick and J. Labadie, Eds., submitted April 1995.

T. Ho, K.J. Wynne, and A.A. Malik, "Polyurethanes Based on a Fluorinated Oxetane Oligomer", *Polymer Preprints Am. Chem. Soc.*, **1995**, 36 (1), 737.

f. Patents:

"Preparation and Polymerization of Initiators Containing Multiple Oxetane Rings: New Routes to Star Polymers"
U.S. Patent No.: 5,362,848 (November 8, 1994).

Inventors: T.G. Archibald; A.A. Malik, G.E. Manser, R.P. Carlson.

"Preparation and Polymerization of Initiators Containing Multiple Oxetane Rings: New Routes to Star Polymers"

Divisional of U.S. Patent No. 5,362,848

U.S. Serial No.: 08/330,480 (Filing Date: January 6, 1995)

Inventors: T.G. Archibald, A.A. Malik, G.E. Manser, R.P. Carlson

"Polymerization of Cyclic Ether Monomers Using Boron Trifluoride Tetrahydrofuranate"

U.S. Patent No.: Granted (June 6, 1995, U.S. Ser. No. 08/226,919).

Inventors: A.A. Malik, T.G. Archibald, G.E. Manser

" Polymers and Copolymers from 3-Azidomethyl-3-nitratomethyloxetane",

U.S. Patent No.: Granted (May 25, 1995, U.S. Serial. No. 07/940,269).

Inventors: G.E. Manser, A.A. Malik, T.G. Archibald.

"3-Azidomethyl-3-nitratomethyloxetane"

Divisional of U.S. Serial No. 07/940,269

U.S. Serial No. 08/469,329 (June 5, 1995).

Inventors: G.E. Manser, A.A. Malik, T.G. Archibald.

"Mono-substituted Fluorinated Oxetane Monomers and Prepolymers, and Methods of Preparation and Polymerization to Produce Fluorinated Elastomers"

Continuation-in-part application of U.S. Serial No.:08/206,859

U.S. Serial No. 08/371, 9914 (Filed on January 11, 1995).

Inventors: A.A. Malik, T.G. Archibald, R.P. Carlson, G. E. Manser, W. L. Harvey

Seven Divisional Applications to U.S. Serial No. 08/371,914 have been filed.

"Fluorinated Diamines and Polymers Formed Therefrom"

U.S. Serial No. : to be issued.

Inventors: A. A. Malik, R.P. Carlson, W.L. Harvey

Presentations:

Malik, A. A. "Fluorinated Polyether-urethanes: Synthesis and Characterization"
Naval Research Laboratory, 25 January 1994.

Malik, A. A. "Novel Fluoroelastomers" Wright Patterson Air Force Laboratory,
Materials Branch, Dayton, Ohio, 04 May 1994

Malik, A. A. "Environmentally Safe Fluoroelastomer Fouling Release Coatings"
Molecular Interactions at Marine Interfaces Contractors Meeting, State University
of New York, Buffalo, 8-10 June 1994.

Malik, A.A. "Preparation and Characterization of Fluoropolymers and Potential
Applications" 3M , July 27, 1994.

Malik, A. A. "Synthesis and Characterization of a New Family of
Fluoroelastomers" University of California, Davis, September 29, 1994

Malik A.A. "Fluoroelastomer Building Blocks", PPG Industries Inc., October 3,
1994.

Malik, A.A. "Fluoropolymer Development at GenCorp Aerojet" Newport News Ship Building, October 5, 1995

Malik, A.A. "Synthesis and Characterization of Novel Fluorinated Polyether Urethane Elastomers" NASA Langley Research Center, Hampton Virginia, October 5, 1995

Malik, A.A. "Fluoropolymer Development at GenCorp Aerojet" Polymer Technologies Inc., October 26, 1995

Malik, A.A. "Careers in Chemistry" University of California, Davis, December 9, 1994

Malik, A.A; Carlson, R.P.; Wynne, K. J.; Ho, T. "Novel Fluorinated Polyether Urethane Elastomers" 12th Winter Fluorine Conference of the American Chemical Society, St. Petersburg, Florida, January 23, 1995

Malik A.A. "Novel Elastomers From Poly Fox Polyols" Bayer Corporation, February 16, 1995

Malik A.A. "Novel Elastomers From Poly Fox Polyols" B.F. Goodrich, February 17, 1995

Malik, A.A. "Environmentally Safe Fluoroelastomer Fouling Release Coatings" Environmentally Safe Ships Meeting, Arlington, Virginia, March 30, 1995.

Ho, T.; Wynne, K.J.; Malik, A.A. "Polyurethanes Based on Fluorinated Oxetane Oligomers", 209th National Meeting of the American Chemical Society, Division of Polymer Chemistry, Anaheim, California, April 1995

Malik, A.A. "Novel Fluorinated Polyether Urethane Elastomers" Baxter Health Corporation, May 23, 1995.

Malik, A. A. "Polymers Based on a Novel Fluorinated Oxetane Soft Block" Molecular Interactions at Marine Interface (MIMI) Meeting, Arlington, Virginia June 23, 1995.

Malik A. A. "Current Issues in Oxetane-based Fluorinated Elastomers" U.S. Patent and Trademark Office, Washington DC, June 27, 1995

c. List of Transitions

Poly Fox urethane elastomers are also useful for variety of applications other applications such as, ice release coatings, stain resistant coatings for carpets and fabrics, high performance paints, adhesive, coatings for glass run channels, automotive coatings, binders for flares and pyrotechnics, and biomedical devices. We are currently working with industry leaders such as 3M, B.F. Goodrich, W.L. Gore & Associates, GenCorp Automotive, Polymer Technology Inc., PPG, Bayer, Korry Electronics, Asahi Glass, and Solvay Chemicals, to develop commercial application for these materials. We are also working with NRL to develop fouling release coatings based on Poly Fox urethanes. In particular, NRL is evaluating Poly Fox urethanes for surface properties and testing it for fouling release in marine environments.